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THE EFFECT OF LEATHER FIBERS ON VULCANIZATION BEHAVIOR OF NATURAL RUBBER

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ABSTRACT

This paper shows the primary research results of the effect of the leather fibers on the vulcanization of natural rubber (NR). The fibers used in this research were prepared by grinding waste leather scraps of Vietnam shoe making company. Leather fibers (LFs) and natural latex rubber were mixed together at various rates by a stirring machine. The obtained composites of natural rubber containing leather fibers were dried at pleasant condition prior to the analysis. Vulcanization behavior of the samples was clarified using a moving die rheometer. The vulcanization temperature as 120 °C is found to be the appropriate temperature for the NR/LFs composite. The increasing of minimum and maximum torque with the increasing of leather fiber content shows the improving in stiffness of natural rubber with the presence of leather fibers. Regarding to curing curves, 40 wt% promises to be the optimal leather fiber content to reinforce natural rubber.

Keywords: natural rubber latex, leather fibers, vulcanization, rheometer.

1. INTRODUCTION

Footwear production has been classified as one of the important industries in Vietnam and many developing countries. However, it is also considered as one of the highly polluting industries, because of the solid waste generated, both from qualitative and quantitative points of view. The main component of solid waste from footwear industry is leather scraps which mainly composed of collagen fibers. Currently, most of the waste is directly sanitary landfill and only small amount is recycled. This is not only caused seriously environmental problem but also wasted a large amount of collagen fiber with many valuable features [1–2]. In recent years, using leather solid waste as an ingredient for new materials have received much attention of many research groups [3–5]. Leather particles have been used as reinforcements for polymer composite materials to modify physical and mechanical properties such as density, hardness, abrasion resistance, tensile strength, flexibility, process ability and so on. Composite materials reinforced by leather wastes are announced to be useful for many industrial applications such as automobile interior, heat insulating boards, shoe soles and construction parts [1, 2]. In this work, vulcanization characteristics of natural rubber (NR) with the presence of leather fibers (LFs) will be investigated. It is one of the most important information for production of the composite material.

2. MATERIALS AND METHODS

2.1. Materials

Natural rubber latex with the dry content of 42% has been used is an industrial type, commercial available and obtained from Vietnamese supplier. Leather fibers were obtained by grinding the grain and corium cow leather scraps generated from a local shoe making company in Hanoi, Vietnam. Average diameter and length of the fibers is 0.1 mm and 10 mm, respectively.

Vulcanization system used in this study includes the basic chemicals which have been widely used in the rubber industry. Vulcanizing agent is dry sulfur powder and auxiliaries that have been used are: zinc oxide (ZnO); stearic acid, tetramethylthiuram disulfide (TMTD), antioxidant RD, vulcanization accelerator DM. All of the vulcanization ingredients were purchased from China chemical suppliers. Moreover, industrial liquid ammonia and acetic acid used in this study were also commercial available types.

2.2. Experimental

Leather fibers and natural rubber latex were mixed together at various compositions by a mechanical stirring machine. All of vulcanization ingredients except for sulfur were simultaneously added to the mixture. The concentration of the chemicals was calculated based on dry rubber content with following proportions: ZnO – 10 %; stearic acid – 4 %; DM – 3 %; TMTD – 3 % and RD – 2 %. 10 ml of aqueous ammonia were added to each sample to avoid premature coagulation. After mixing, an appropriate amount of acetic acid was poured onto the mixtures in order to coagulate them completely. The obtained master batches were washed by water for neutralization and then pleasant dried at 70 °C for 8 – 10 hours to remove all excess water. Then, the mixture and sulfur powders were compounded by a laboratory scale two roll mill machine. The concentration of sulfur powder was 5 % to the dry rubber content. Obtained flat sheets of final composites with 1.5 mm in thickness were used for vulcanization and rheological analysis.

2.3. Measurement

Vulcanization characteristics of the composites were investigated at difference temperatures in order to determine the maximum (MH) and minimum (ML) torques, scorch time (ts), and optimum curing time (t90). Measurement procedure was followed the ISO 6502:2016 standard using a rotorless rheometer testing (RLR–4, Japan). The pressure was kept at 10 MPa and frequency was 100 cpm for all samples. All of the measurements were conducted at Center of Rubber Science and Technology, Hanoi University of Science and Technology.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on natural rubber vulcanization

As protein nature, leather fibers are much affected by temperature [6]. Therefore, the vulcanization temperature of the composite materials has to be suitable to endurance of the leather fibers. It has to be enough to vulcanize the rubber but should not be so high, which can lead to the thermal degradation of the fibers. For those reasons, three vulcanization temperatures were chosen for investigating are 110 °C, 120 °C and 130 °C. The results in Figure 1 and Figure 2 show the effect of vulcanization temperature on rheology and the vulcanization time of the natural rubber system.

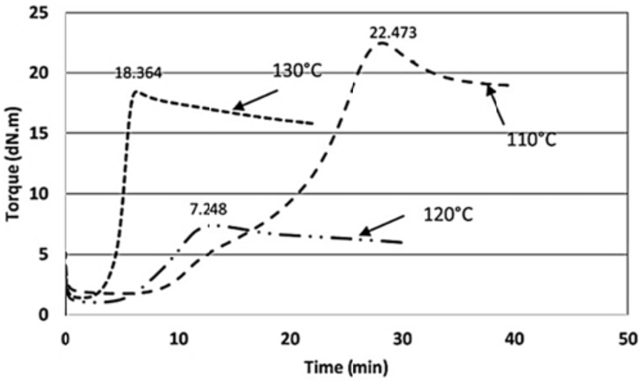

Figure 1. Effect of vulcanization temperature on rheology.

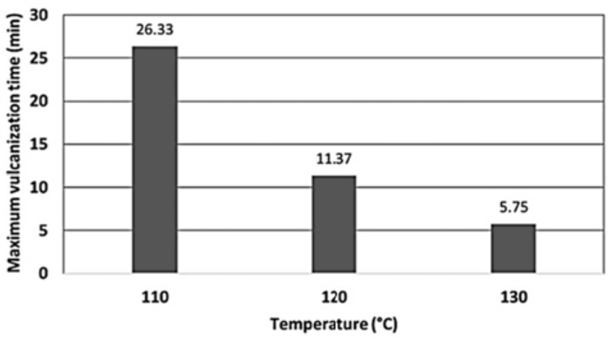

Figure 2. Effect of vulcanization temperature in vulcanization time.

As can be seen in Figure 2, the maximum vulcanization time is decreased with the increasing of temperature. But on the other hand, at 130 °C the vulcanization of natural rubber is two fast that lead to the suddenly increasing of torque as shown in Figure 1 (NR system reached the maximum torque in approximately 5 minutes). This fact will cause the difficult in leather fiber dispersion into NR. However, the long time in high temperature can also cause the thermal degradation of leather fiber. Hence, staying in 110 °C in approximately 27 minutes to reach the maximum vulcanization of NR is not good for leather fiber. It can be seen very clearly in the decreasing of maximum torque, which supposed to be the thermal degradation. For those reasons, 120 °C seem to be the appropriate vulcanization temperature for the NR/LFs composite system.

3.2. Effect of leather fiber content on rheology of NR/LFs composite

Effect of leather fiber on rheology of NR/LFs composite was evaluated by curing curves of NR/LFs systems with various fibers content such as 20, 30, 40, 50 wt%, respectively.

The point of inflection upward from the minimum torque is an indication of the onset of vulcanization and the corresponding period (scorch time) is very crucial for the safe processing of the rubber compound at the selected temperature. The maximum torque in the curing curve indicates the completion of vulcanization and the time to reach 90% of the maximum torque is taken as the optimum curing time. The nature of the curing curve after reaching the maximum torque is an indication of the stability of the polymer and of the crosslinks introduced. If there is no change in the torque as a function of time after reaching the maximum value, the cure is plateau in nature and if it increases continuously with respect to time it is referred to as marching cure. On the other hand, if the torque decreases from the maximum, it is referred to as reversion, an indication of thermo–oxidative degradation of the polymer network and the crosslinks introduced therein.

When leather was added into NR, the minimum and maximum torque values were found to be higher than pure NR (Figure 3 and Figure 4). The increasing of the compound stiffness could be due to the fibrous and rigid nature of the leather irrespective of the dilution of the curatives in the matrix.

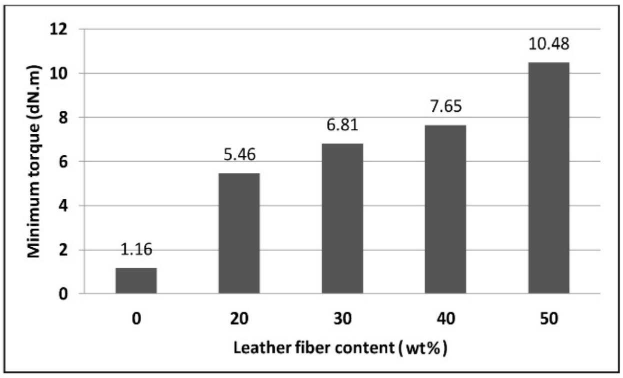

Figure 3. Effect of LFs on minimum torque.

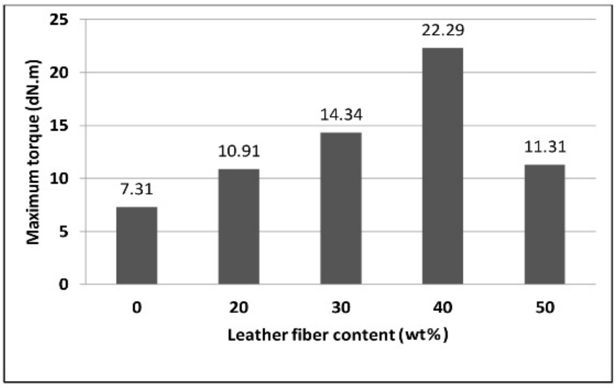

Figure 4. Effect of LFs on maximum torque.

As can be seen in Figure 5, in the case of NR compound without leather fiber, no reversion is observed up to 15 minutes. On the contrary, NR/LFs compound is found to exhibit reversion earlier with the increasing of LFs content (Figure 5). This can be supposed because of the presence of LFs incorporated in NR system.

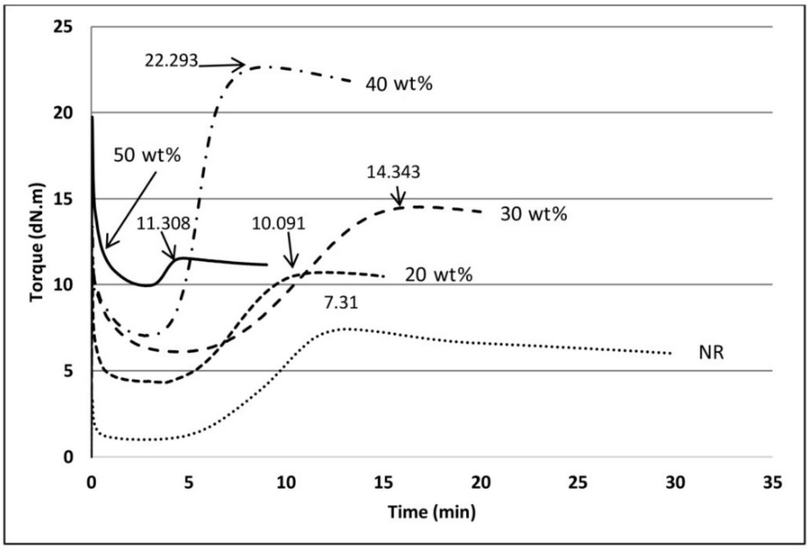

Figure 5. Curing curves of NR/LFs composite materials.

Furthermore, NR/LFs composite materials show the decreasing of maximum torque with 50 wt% of LFs. It could be referred to the high volume content of LFs in NR/LFs compound leads to the phase separation of NR in the composite system. Regarding to Figure 5, the LFs content of 40 wt% could be the good LFs content for NR/LFs composite materials.

4. CONCLUSIONS

The vulcanization of natural rubber was investigated at difference temperatures using a rotorless rheometer testing. It is found that appropriate temperature for vulcanization of NR/LFs composite system should be 120 °C. Moreover, it is clarified that the presence of LFs leading to the decreasing of the vulcanization time and increasing of maximum torque of NR. This finding indicates the stiffening of the composite materials because of rigid and fibrous nature of leather. The experimental results also suggest that 40 wt% seem to be the optimal content of leather fibers for manufacturing of NR/LFs composite. However, futher microstructure investigation and mechanical analysis will be required to verify and affirm this conclusion. The information gained from this study is the scientific basis for the design and manufacture of new material from waste leather fibers, contributing to creating added value and reducing environmental pollution of leather and footwear industry.

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